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Kinetic Theory of Field Evaporation of Metals

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Abstract - Starting from adiabatic energy curves, calculated as a function of electric field strength we develop a perturbational method to construct diabatic states which form the basis to compute the temperature dependent ionization probabilities for field evaporation of metals. Employing a master equation we calculate the energy dependent ion yield as a function of field strength and temperature, and extract the field dependence of the activation barrier and the prefactor. As a function of field strength the activation barrier for field evaporation decreases monotonically for tungsten, whereas the prefactor increases up to a field strength of  $4.5\text{V}/\text{\AA}$  for tungsten due to an increase in the ionization probability and then decreases due to changes in the surface potential.

## 1. Introduction

Field evaporation is the removal of lattice atoms from the surface of a field emitter tip as singly or multiply charged positive ions in an electric field of the order of volts per angstroms [1,2]. The term field desorption is usually reserved for the process of removing field-adsorbed atoms or molecules from field emitter tips [3-5]. Field evaporation and field desorption, crucial in cleaning and preparing field emitter tips, are thermally activated processes; as such their rate constants can be parametrized as

$$r_d = \alpha \nu \exp(-Q(F)/k_B T) \quad (1)$$

Here  $Q(F)$  is the field dependent height of the activation barrier to be overcome by the desorbing particle. We have split the prefactor into an attempt frequency  $\nu$  and an accommodation coefficient  $\alpha$ , both being field and also weakly temperature dependent. The minimum field strength beyond which the activation barrier vanishes, thus leading to field evaporation at low temperatures, is called the evaporation field strength; it varies from 2.5V/Å for Ti to 6.1V/Å for W with a typical experimental error margin of 10-20 % [5]. Ernst has measured  $Q(F)$  and  $\alpha \nu(F)$  for Rh [6], and Kellogg [7] has presented data for W in the field range 4.7-5.9V/Å.

Two phenomenological models have been proposed to calculate the activation energy  $Q(F)$ . In the "image-force" model [2] field evaporation is envisaged as the activation of an ion of charge  $ne$  over an activation barrier that results from the superposition of the field potential  $-neFz$  (assuming a constant electric field), and the image potential of the ion  $-ne/4z$ . In the "charge-exchange" model [8] one assumes that ionization and desorption occurs at the crossover point between the atomic and ionic (diabatic) potential energy curves. A confrontation of these models with experimental data has been presented by Kellogg [7]; Forbes [9] has presented several critical assessments. An early microscopic calculation of  $Q(F)$  by Kahn and Ying [10] was based on the local density approximation of the density functional theory, treating the metal as a jellium. Kingham [11] has presented some preliminary results for the field evaporation of W obtained within a tight binding cluster model. Kreuzer and Nath [12] have presented a microscopic theory of field evaporation in which the electronic properties of the metal are calculated within a tight binding cluster approach based on the ASED-MO method [13] with local electric fields taken from selfconsistent jellium calculations [14,15]. They extract the activation energy  $Q(F)$  from adiabatic ground state energy curves, and find a scaling law which predicts evaporation field strengths within 10%-20% of experimental values.

To extend such ground state energy calculations to a kinetic theory of field desorption and evaporation, Kreuzer et al. [16-18] have employed a master equation to calculate the energy dependent ion yield in thermal field desorption as a function of field strength and temperature, applying their method to thermal field desorption of helium. In this paper we will briefly review this theory and then use it to study field evaporation of metals.

In the next section we will review the calculation of adiabatic and diabatic energy curves in the presence of high electric fields at surfaces. The latter will then serve as the framework to compute the temperature dependent ionization and neutralization probabilities of atoms on the surface of a metal. In the last section we will present numerical data for field evaporation of W. To summarize our results: we find, as in our earlier study [12], that the activation barrier against field evaporation decreases (monotonically for most metals, such as tungsten, for which we find good agreement with Kellogg's data [7]) whereas the prefactor initially increases (up to 4.5V/Å for tungsten) due to an increase in the ionization probability, and then decreases due to changes in the surface potential of the desorbing atom.

## 2. Adiabatic and diabatic states

Field evaporation takes place predominantly at kink and step sites due to the fact that electric fields are enhanced at such sites. To set up our theory we rather consider a situation where a single metal atom is present on top an otherwise perfect crystal plane, a distance  $R$  away from the topmost ion cores. We will refer to this isolated atom as the adatom. The hamiltonian of the system can be written as

$$H = T_N + H_e(r_1, r_2, \dots; R) \quad (2)$$

where

$$T_N = -\frac{\hbar^2}{2M} \partial^2 / \partial R^2 \quad (3)$$

is the kinetic energy of the atomic nucleus and

$$H_e = -\frac{\hbar^2}{2m} \sum_n \frac{\partial^2}{\partial r_n^2} + V_e(r_1, r_2, \dots; R) \quad (4)$$

is the hamiltonian of the electrons at positions  $r_1, r_2, \dots$ .  $V_e$  includes the Coulomb interactions between the electrons, between the electrons and the nuclei, and between all nuclei (metallic and atomic).

Let us fix the position of the adatom, thus setting its kinetic energy (3) equal to zero. Physically this implies that the electronic degrees of freedom follow the nuclear motion instantly. We can then diagonalize  $H_e$  (in practice, after approximating it, e.g., by a tight binding hamiltonian or using density functional theory) to obtain

$$H_e(r_1, r_2, \dots; R) \zeta_i(r_1, r_2, \dots; R) = V_i(R) \zeta_i(r_1, r_2, \dots; R) \quad (5)$$

where the  $\zeta_i$  are adiabatic many electron wavefunctions. The lowest eigenvalue of (5),  $V_0(R)$  represents the ground state of the system and corresponds to the adiabatic binding energy curve. Lifting an electron from the highest occupied level (in the ground state) to the lowest unoccupied one, generates the energy curve (or rather surface, because  $R$  is a three-dimensional space coordinate) of the first excited state etc.

To take the nuclear motion of the adatom into account we now proceed to construct diabatic states. Returning to the hamiltonian (2) we try to diagonalize it by solving Schrödinger's equation

$$H \Psi_\alpha = E_\alpha \Psi_\alpha \quad (6)$$

via an expansion

$$\Psi_\alpha(r_1, r_2, \dots; R) = \sum_i \zeta_i(r_1, r_2, \dots; R) \chi_{i\alpha}(R). \quad (7)$$

Inserting (7) into (6), multiplying with  $\zeta_i^*$  and integrating over the electronic degrees of freedom,  $r_1, r_2, \dots$ , we obtain a coupled set of equations

$$\left[ -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2} + V_i(R) - E_\alpha \right] \chi_{i\alpha}(R) = \frac{\hbar^2}{2M} \sum_j (T_{ij}^{(2)} + 2 T_{ij}^{(1)} \frac{\partial}{\partial R}) \chi_{j\alpha} \quad (8)$$

where

$$T_{ij}^{(1)}(R) = \int \zeta_i^*(r_1, r_2, \dots; R) \frac{\partial}{\partial R} \zeta_j(r_1, r_2, \dots; R) dr_1 dr_2 \dots \quad (9)$$

$$T_{ij}^{(2)}(R) = \int \zeta_i^*(r_1, r_2, \dots; R) \frac{\partial^2}{\partial R^2} \zeta_j(r_1, r_2, \dots; R) dr_1 dr_2 \dots \quad (10)$$

are the matrix elements of the first and second order differential operators. Putting the right hand side equal to zero results in the Born-Oppenheimer approximation according to which the nucleus just moves in the  $i$ -th adiabatic potential.

To solve (8) amounts to obtaining an exact solution to the problem by diagonalizing an infinite matrix. To reduce the task to manageable proportions one hopes that in a given problem only a limited number of adiabatic states contribute to the set of diabatic states involved in the process to be studied. E.g. in field desorption and field evaporation, only the lowest diabatic states for a neutral atom and for ions seem important. They can thus be obtained by a unitary transformation from the corresponding adiabatic states. The latter being known explicitly from the tight binding or density functional calculations alluded to above, the problem is solved in practice.

Let us introduce new states

$$\chi = \underline{A} \eta \quad (11)$$

where  $\chi^T = (\chi_1, \chi_2, \dots)$  is the transpose of the column vector  $\chi$  containing the adiabatic states as its components and  $\underline{A}$  is a unitary matrix which is an explicit function of  $R$ . To obtain a diabatic solution of (8) we choose the transformation  $\underline{A}$  such that the first order derivative term vanishes, i.e. we impose the condition [19]

$$\left( \frac{\partial}{\partial R} + \underline{T}^{(1)} \right) \underline{A} = 0 \quad (12)$$

We thus get from (8)

$$\left( -\frac{\hbar^2}{2M} \underline{I} \frac{\partial^2}{\partial R^2} + \underline{W}(R) - \underline{E} \right) \eta = 0 \quad (13)$$

where  $\eta$  are diabatic states. In (13)  $\underline{I}$  is a unit matrix,  $\underline{E}$  is diagonal and the diabatic interaction matrix, no longer diagonal, is given by

$$\underline{W} = \underline{A}^\dagger \underline{V} \underline{A} \quad (14)$$

in terms of the adiabatic energy curves defined in (5). Dropping the coupling terms  $W_{ij}$  from (13) determines uncoupled diabatic states subject to

$$\left( -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2} + W_{ii}(R) - E_{i\nu} \right) \eta_{i\nu} = 0 \quad (15)$$

Thus  $\eta_{iv}^0$  is the  $v$ th eigenstate with energy  $E_{iv}$  of the  $i$ th diabatic potential  $W_{ii}(R)$ . E.g.  $W_{00}$  would be the potential for a neutral atom approaching a surface, and  $W_{11}$  that of an ion. The off-diagonal terms  $W_{ij}$  couple these states together; in the above example,  $W_{01}$  is responsible for ionization or neutralization.

Combining (7) and (11), we can rewrite the total wavefunction as

$$\begin{aligned}\Psi(r;R) &= \zeta^T(r;R)\chi(R) \\ &= \zeta^T(r;R)A(R)\eta(R) \\ &= \xi^T(r;R)\bar{\eta}(R)\end{aligned}\tag{16}$$

introducing the diabatic many electron wavefunctions,  $\xi^T(r;R)=(\xi_0, \xi_1, \dots)$ .

Before we continue with the explicit calculation of adiabatic and diabatic states, we want to briefly discuss the meaning of these states. To this end we assume that in the process of field desorption or field evaporation only two levels participate with the lower electronic states remaining unchanged as spectators throughout the process. We denote by  $\phi_a$  the highest occupied single electron level with energy  $\epsilon_a$  in the isolated adatom and by  $\phi_m$  the lowest unoccupied level of the same symmetry with energy  $\epsilon_m$  above the Fermi energy of the isolated metal. In the interacting system of adatom plus metal these two levels combine to two molecular orbitals  $\phi_g$  and  $\phi_e$  of lower and higher energy, respectively, see Fig.1. Assuming that we can approximate the adiabatic many electron wavefunctions as Slater determinants, we find that the adiabatic ground state wavefunction for  $N$  electrons

$$\zeta_0(r;R) = |\phi_1\phi_2\cdots\phi_{N-1}\phi_g|\tag{17}$$

is composed of the spectator states,  $\phi_i$  for  $i=1, \dots, N-1$ , and  $\phi_g$ , whereas the lowest excited many electron wavefunction

$$\zeta_1(r;R) = |\phi_1\phi_2\cdots\phi_{N-1}\phi_e|\tag{18}$$

has  $\phi_g$  replaced by  $\phi_e$ . Assuming that with the adatom close to the metal  $\epsilon_a$  is lower than  $\epsilon_m$ ,  $\phi_g$  and  $\phi_e$  are dominated by  $\phi_a$  and  $\phi_m$ , respectively. Thus  $\zeta_0$  represents a many electron state in which both adatom and metal are in their respective neutral ground states, whereas  $\zeta_1$  describes a situation with an electron removed from the adatom and put onto the metal.

We next look at a situation where, in the presence of an electric field the adatom is so far away from the surface that  $\epsilon_a$  is higher than  $\epsilon_m$ . As a result the molecular orbital  $\phi_g$  is now mainly of  $\phi_m$  character, whereas  $\phi_e$  is mostly  $\phi_a$ , implying that  $\zeta_0$  now describes a system with the adatom being ionic and the removed electron in the metal above the Fermi energy, whereas  $\zeta_1$  represents neutral adatom and metal.

In our previous paper [18] we had shown that for two relevant states the transformation  $A$  in (11) can be represented by a unitary  $2 \times 2$  matrix which can be written, quite generally, as

$$\underline{A} = \begin{bmatrix} \cos\theta(R) & \sin\theta(R) \\ -\sin\theta(R) & \cos\theta(R) \end{bmatrix}.\tag{19}$$

Noting that the matrix  $\underline{T}^{(1)}$  is antisymmetric, we reduce the matrix equation (12) to a simple vector equation

$$\frac{\partial}{\partial R} \Theta(R) = - \langle \xi_0 | \frac{\partial}{\partial R} \xi_1 \rangle = - \int d\mathbf{r}_1 d\mathbf{r}_2 \dots \xi_0^*(\mathbf{r}_1, \mathbf{r}_2, \dots; R) \frac{\partial}{\partial R} \xi_1(\mathbf{r}_1, \mathbf{r}_2, \dots; R) \quad (20)$$

which can be solved as a line integral

$$\Theta(R) = - \int_{R_0}^R dR' \cdot \langle \xi_0 | \frac{\partial}{\partial R'} \xi_1 \rangle . \quad (21)$$

Having  $\Theta(R_0)=0$  implies that  $A(R_0)=I$  and thus that at  $R_0$  diabatic and adiabatic states coincide which is the case far from the surface. The diabatic interaction matrix (14) is now given explicitly by its components

$$W_{00}(R) = \cos^2 \Theta(R) V_0(R) + \sin^2 \Theta(R) V_1(R) \quad (22)$$

$$W_{11}(R) = \cos^2 \Theta(R) V_1(R) + \sin^2 \Theta(R) V_0(R) \quad (23)$$

$$W_{01}(R) = \frac{1}{2} \sin 2\Theta(R) [V_0(R) - V_1(R)] . \quad (24)$$

To evaluate (21), we observed that in field desorption adatoms will leave the surface along the steepest field gradient, i.e. perpendicular to the surface so that we can neglect any lateral interactions and  $\Theta=\Theta(z)$  depends on the distance  $z$  from the metal only so that

$$\Theta(z) = \int_{\infty}^z dz \int d\mathbf{r} \phi_g(\mathbf{r}; z) \partial/\partial z \phi_e(\mathbf{r}; z) \quad (25)$$

provided that the adiabatic many electron wavefunctions are given by Slater determinants. This completes the construction of diabatic states for situations where two states are important. We should note, however, that even in the case of thermal field desorption of helium, this is not strictly true. Recall that field ionization of the adatom can take place when its highest occupied level rises above the lowest unoccupied level in the metal. For a given field strength,  $F$ , this happens, if the adatom is at a distance  $z_0(F)$ . If the desorbing atom is at distances  $z$  larger than  $z_0$ , the electron can tunnel into higher unoccupied levels of the metal. Thus for given  $F$  and  $z$ , only two states participate in the ionization process and thus in the construction of diabatic states, although for the overall field desorption process a band of metal states is relevant. Note, however that, because the tunneling probability decreases rapidly as a function of distance, this band of tunneling states is rather narrow. Mimicking the metal by a finite cluster of metal atoms obviously does not produce a band structure but only a set of discrete levels which one has to broaden with a width corresponding to the width of the ionization zone

Dealing with thermal field evaporation of metal ions, the situation becomes more complex because it is less evident how to assign molecular orbitals of the metal plus adatom complex to either the adatom or the metal, particularly if the latter is approximated by a finite cluster itself. Many states then become important corresponding to different stages of ionization and, more importantly, of different outgoing momentum. In principle, we can use the above formalism resulting in the construction of large matrices  $A$ . Instead, we will advance a perturbative approach to the construction of diabatic states that starts from the observation that the



transfer of an electron from the adatom to the metal takes place when the highest occupied level on the adatom rises above the Fermi level of the metal. If this happens with the adatom at position  $z_0$ , we can linearize the energy of the highest occupied level as

$$\epsilon_a(z) = \epsilon_m + \Delta\epsilon(z) \quad (26)$$

with  $\Delta\epsilon(z_0) = 0$ . We further write for the molecular orbitals, restricting ourselves to two levels for the moment,

$$\begin{aligned} \phi_g &= c_{gm}\phi_m + c_{ga}\phi_a \\ \phi_e &= c_{em}\phi_m + c_{ea}\phi_a \end{aligned} \quad (27)$$

and get to second order

$$\begin{aligned} c_{gm} &= \frac{1}{\sqrt{2}} \frac{1-(f-g)S}{\sqrt{1+f^2-fg}} \\ c_{ga} &= \frac{1}{\sqrt{2}} \frac{f-g}{\sqrt{1+f^2-fg}} \\ c_{em} &= \frac{1}{\sqrt{2}} \frac{1-(f+g)S}{\sqrt{1+f^2+g}} \\ c_{gm} &= \frac{1}{\sqrt{2}} \frac{f+g}{\sqrt{1+f^2+g}} \end{aligned} \quad (28)$$

where

$$\begin{aligned} f(z) &= \Delta\epsilon(z)/(2(V-\epsilon_m S)) \\ g &= \sqrt{1+f^2} \\ V &= \langle \phi_m | h | \phi_a \rangle \\ S &= \langle \phi_m | \phi_a \rangle \end{aligned} \quad (29)$$

The transformation angle (25) is then given by

$$\theta(z) = \frac{1}{2} \text{tg}^{-1} f(z) - \pi/4 \quad (30)$$

where  $h$  is the single electron hamiltonian. Having  $\theta(z)$ , we can next calculate the diabatic potentials  $W_{ij}$  from (22-24). In particular, note that

$$V_0 - V_1 = -g(V - \epsilon_m S) \quad (31)$$

so that

$$W_{01}(z) = V(z) - \epsilon_m S(z) \quad (32)$$

The diabatic many electron wave functions are then given by

$$\begin{aligned} \xi_0(\mathbf{r}; R) &= (c_{gm} \cos \theta - c_{em} \sin \theta) |\phi_1 \phi_2 \dots \phi_{N-1} \phi_m| \\ &\quad + (c_{ga} \cos \theta - c_{ea} \sin \theta) |\phi_1 \phi_2 \dots \phi_{N-1} \phi_a| \\ \xi_1(\mathbf{r}; R) &= (c_{gm} \sin \theta + c_{em} \cos \theta) |\phi_1 \phi_2 \dots \phi_{N-1} \phi_m| \\ &\quad + (c_{ga} \sin \theta + c_{ea} \cos \theta) |\phi_1 \phi_2 \dots \phi_{N-1} \phi_a| \end{aligned} \quad (33)$$

where, with (30),

$$\begin{aligned} \sin \theta(z) &= -\sqrt{1-f/g} \\ \cos \theta(z) &= \sqrt{1+f/g} \end{aligned} \quad (34)$$

so that (33) reduces, properly normalized, to

$$\begin{aligned} \xi_0(\mathbf{r}; R) &= (1-S^2)^{-1/2} (|\phi_1 \phi_2 \dots \phi_{N-1} \phi_a| - S |\phi_1 \phi_2 \dots \phi_{N-1} \phi_m|) \\ \xi_1(\mathbf{r}; R) &= |\phi_1 \phi_2 \dots \phi_{N-1} \phi_m| \end{aligned} \quad (35)$$

where  $S$  is the overlap of levels  $\phi_a$  and  $\phi_m$ , as given in (29).

To assess this perturbative approach we have recalculated a few numbers relevant for field desorption of helium from tungsten. E.g., in a field of  $5.5 \text{ V/\AA}$   $W_{01}(z_c) = 1.96 \text{ meV}$  using the exact transformation and  $1.78 \text{ meV}$  employing the approximate formula (32). In the relevant interval of  $z$  around  $z_c$  the error is never larger than 30%.

We now want to generalize the perturbative approach to situations where several, or many states on the adatom and in the metal participate in the ionization process. We first rewrite the interaction matrix of the hamiltonian in the diabatic basis as

$$\underline{W}(R) = \int d\mathbf{r} \underline{\xi}(\mathbf{r}; R) H_e(\mathbf{r}; R) \underline{\xi}^T(\mathbf{r}; R) \quad (35)$$

and assume again that the many electron wave functions can be approximated by single Slater determinants. We denote by  $\phi_a$  the wave function of the highest occupied level on the isolated atom and by  $\phi_{m,k}$  with  $k=1,2,\dots$  single electron wave functions of energy  $\epsilon_{m,k}$  above the Fermi level of the isolated metal. To ensure orthogonality, we define

$$|\tilde{\phi}_a\rangle = N_a \hat{P}_m |\phi_a\rangle \quad (36)$$

where the projection operator is given by

$$\hat{P}_m = 1 - \sum_k |\phi_{m,k}\rangle \langle \phi_{m,k}| \quad (37)$$

so that the normalization constant becomes

$$N_a^{-2} = 1 \cdot \sum_k \langle \phi_{m,k} | \phi_a \rangle^2 \quad (38)$$

The diabatic many electron wave function of lowest energy with both adatom and metal neutral is then given by

$$\xi_0(\mathbf{r}; \mathbf{R}) = |\phi_1 \phi_2 \dots \phi_{N-1} \phi_a| \quad (39)$$

The excited states are described by

$$\xi_k(\mathbf{r}; \mathbf{R}) = |\phi_1 \phi_2 \dots \phi_{N-1} \phi_{m,k}| \quad (40)$$

having one electron transferred from the adatom to the  $k$ -th level above the Fermi energy of the metal. Writing the electronic hamiltonian as a sum of single electron contributions

$$H_e(\mathbf{r}; \mathbf{R}) = \sum_{i=1}^N h(\mathbf{r}_i; \mathbf{R}) \quad (41)$$

and inserting (39) and (40) into (35) we get for the offdiagonal terms

$$W_{0k}(\mathbf{R}) = N_a (V_k - \epsilon_{m,k} S_k) \quad (41)$$

where

$$V_k = \langle \phi_a | h | \phi_{m,k} \rangle \quad (42)$$

is the interaction between states  $\phi_a$  and  $\phi_{m,k}$ , and

$$S_k = \langle \phi_a | \phi_{m,k} \rangle \quad (43)$$

is the overlap between them. This completes the perturbative approach to the calculation of the diabatic interaction matrix (35).

## 5. Results

In our previous paper [18] we have outlined the derivation of kinetic equations that control field ionization, field desorption and field evaporation. In particular, we derived an expression for the yield of singly charged ions

$$Y_{ion} = \sum_{\nu, \mu} T_{0+}(\mu, \nu) \exp(-E_{0\mu}/k_B T) / \sum_{\mu} \exp(-E_{0\mu}/k_B T) \quad (44)$$

where [20]

$$T_{ij}(\nu, \mu) = 2\pi/\hbar \left| \int d\mathbf{R} \, \eta_{1\nu}^{0*}(\mathbf{R}) W_{ij}(\mathbf{R}) \eta_{j\mu}^0(\mathbf{R}) \right|^2 \Delta(E_{i\nu} - E_{j\mu}, \Gamma_{j\mu}) \quad (45)$$

with

$$\Delta(\epsilon, \Gamma) = \pi^{-1} (\Gamma/2) / (\epsilon^2 + \Gamma^2/4) \quad (46)$$

Here  $\Gamma_{j\mu}$  is the half width of level  $\mu$  in  $W_{jj}$  due to phonon transitions. Because  $T(i\nu, j\mu)$  describes transitions between discrete states of the unperturbed hamiltonian, care must be exercised to include the width of the initial state. This is done formally by replacing the energy conserving  $\delta$ -function by the Lorentzian (46).

We will now report on numerical results on thermal field evaporation of tungsten ions from a tungsten tip. The latter we model by a finite size cluster of tungsten atoms, which, to mimick an isolated atom on a (111) surface, is chosen as three atoms in a plane with one atom below the midpoint of the triangle, and a fifth one in the symmetrical position above the plane. Our calculations are based on the semi-empirical ASED-MO method, described in earlier papers [12, 18]; ionization energies and wavefunctions for W are those of Ref.[12] except that we have raised, in an ad hoc manner, the ionization energies for the adatom by 1.5eV so that we can describe by one set of parameters both the neutral and ionic state of this atom. In this approach we unfortunately cannot incorporate the electric field in a selfconsistent manner. However, because the local variation of the electric field is important, we take the electric field from selfconsistent calculations [14,15] for a plane jellium metal using density functional theory assigning a Wigner-Seitz radius  $r_s=2.07$  to tungsten. We then impose this field onto the cluster assuming that the jellium edge is half a lattice spacing above the plane of atoms in our cluster.

To determine the transition probabilities (45) we must know the nuclear wave functions,  $\psi_{0\nu}$  and  $\psi_{1\mu}$ , in the diabatic potentials,  $W_{00}$  and  $W_{11}$ . To simplify the numerics we have fitted a Morse potential to  $W_{00}$ , i.e.

$$W_{00}(z) = A_0(F) [\exp[-2Y(z-z_0)] - 2\exp[-Y(z-z_0)]] \quad (47)$$

adjusting its parameters,  $A_0(F)$ ,  $Y(F)$  and  $z_0(F)$ , as a function of field strength. Likewise, we set

$$W_{11}(z) = W_0 - eF(z-z_0) \quad (48)$$

for the diabatic curve of the ion. For both potentials the wave functions can be given analytically.

Field evaporation being an activated process, it is instructive to parametrize the ion yield rate constant according to the Polanyi-Wigner equation (1). In Table I we present the relevant data. We note first that the activation energies for field evaporation,  $Q(F)$ , are in good agreement with experiment. To put this into perspective, we want to point out that this agreement depends on our choice for  $r_s$ , as discussed in [1], e.g. if we take  $r_s=1.5$  the calculated evaporation field strength increases by about 25% from its value at  $r_s=2.07$ .

Turning next to the prefactor  $\nu(F)$  we first note its dependence on field strength. In the early days of field ion spectroscopy it had been assumed that the prefactor is independent of field strength [21]. However, Kellogg [7] has found a substantial field dependence in field evaporation of tungsten. For thermal field desorption of helium our theory [18] explained such a field dependence as the result of the changes in the shape of the surface potential in which helium is adsorbed. For field evaporation this effect is also present albeit of lesser significance. To obtain a better understanding, we recall that in thermal desorption in the absence of a field, the desorption rate constant at low coverage can be written for desorption from a mobile, nonlocalized adsorbate as

$$r_d = S\nu_z \exp(-E_d/k_B T) \quad (49)$$

when  $h\nu_z \ll k_B T$ , and as

$$r_d = S k_B T / h \exp(-E_d / k_B T) \quad (50)$$

when  $h\nu_z \gg k_B T$ . From a localized adsorbate we get

$$r_d = S 2\sqrt{m a_s} / k_B T \nu_x \nu_y \nu_z \exp(-E_d / k_B T) \quad (51)$$

where  $\nu_x$  etc. are the vibrational frequencies of the adsorbed particle at the bottom of the surface potential well in the x, y, and z directions. Note that the desorption rate also contains, due to detailed balance, the sticking coefficient S as a measure of the efficiency of energy transfer between the solid and the adatom.

For field desorption and field evaporation the adatom must be thermally excited up to the energy of the potential barrier; this is a process akin to thermal desorption. Subsequently, it must get ionized. Thus the prefactor consists of two factors, namely an ionization probability  $\alpha(F)$  and an attempt frequency  $\nu(F)$ . Their field dependences are opposing each other in that  $\alpha(F)$  increases from zero in zero field to one at "high" fields, whereas  $\nu(F)$  decreases. We can view this process as a particle localized in the excited level,  $\epsilon_i = Q(F)$ , at the energy of the potential barrier attempting with a frequency  $\nu_i = \epsilon_i / h$  of that level to ionize with a probability  $\alpha(F)$ . Because  $Q(F)$  decreases with F, so does  $\epsilon_i$  and thus  $\nu_i$ . In addition, the hump of the activation barrier and thus the region for ionization moves towards the metal for increasing field resulting in an increasing ionization probability  $\alpha(F)$ . In Table 1 we have estimated the critical energy level in  $W_{00}$ , assumed to be a Morse potential, and find that e.g. for  $F = 4.7 \text{ V/\AA}$  the adatom is in the 37th excited state when it attempts to ionize. This level has a frequency  $\nu_{37} = 2.86 \times 10^{14} \text{ s}^{-1}$  as opposed to the ground state frequency  $\nu_0 = 4.5 \times 10^{12} \text{ s}^{-1}$ . This compares rather well with the prefactor of  $2.76 \times 10^{14} \text{ s}^{-1}$  obtained from the Polanyi-Wigner parametrization of the ion yield. This argument should, however, not be taken too literally as other factors contribute to the prefactor as one already knows from the simpler situation of thermal desorption, cf. equations (49-51). In particular this estimate does not allow us to extract  $\alpha(F)$  because it would obviously be larger than one, contrary to its definition. However, we can guess that for fields less than  $4.5 \text{ V/\AA}$  the field dependence of  $\alpha(F)$  dominates, and most likely  $\alpha(F) = 1$  for larger fields, where the decrease in  $\nu(F)$  becomes dominant.

Although our theory produces the right trend in the prefactor, namely decreasing with increasing field for fields larger than  $4.5 \text{ V/\AA}$ , as observed by Kellogg, there are discrepancies in the absolute values in that the experimental data are substantially lower except at  $F = 4.7 \text{ V/\AA}$ . However, Kellogg warns that his prefactors have an uncertainty of at least one order of magnitude. On the other hand, our theoretical values may also be out by an order of magnitude due to several of our approximations, in particular neglecting lateral variations in the electric field which might effect the localization of the adatom. Also recall that the master equation that underlies (44) as derived in refs. [16,18], is restricted in its applicability to the markovian limit. With prefactors of the same order ( $10^{14} \text{ s}^{-1}$ ) as thermal phonon assisted transitions in  $W_{00}$ , one should account for nonmarkovian effects by, e.g., using the Tsukada-Gortel equations [20], which will result in lower prefactors, but most likely not more than one order of magnitude.

We would like to comment further on the difference in prefactors for field evaporation of tungsten as opposed to thermal field desorption of helium. For the latter case we found [18] prefactors increasing more or less exponentially from a low of  $10^6 \text{ s}^{-1}$  at  $F = 4 \text{ V/\AA}$  to a high of  $10^{12} \text{ s}^{-1}$  at  $6 \text{ V/\AA}$ . This has been interpreted as due to an increase in the ionization probability  $\alpha(F)$  due to rapidly increasing overlap of wave functions on the helium and in the metal. After all, in the same field strength

regime the activation barrier for helium increases substantially whereas for metal field evaporation the activation barrier decreases monotonically, i.e. for helium the field enhances adsorption, at least up to  $6\text{V}/\text{\AA}$ . Eventually, this enhancement ceases, most likely around  $7\text{V}/\text{\AA}$  due to the same effects that cause a monotonic weakening of the surface bond for metals on metals, namely a draining of bonding orbitals into the metal.

We have so far presented results on thermal field evaporation of singly charged tungsten ions. Experiment, on the other hand, only detects  $\text{W}^{3+}$  and  $\text{W}^{4+}$  ions. The fact that our calculated prefactors are rather large, i.e. of the order of  $10^{14}\text{s}^{-1}$ , we take as evidence to suggest that the first ionization stage from  $\text{W}$  to  $\text{W}^+$  must be the slowest, i.e. rate determining step. Because the tunneling rate into the metal decreases rapidly with increasing distance, the higher ionization states cannot be produced by tunneling into the metal as their abundance would in that case be decreased over singly charged ions roughly by the ratio of the ionization rates. Thus post ionization [24] happens at least several angstroms away from the surface, but still in the high field region, by field ionization with the excess electrons tunneling into vacuum states rather than into empty metal states. Simple minded estimates confirm this scenario although detailed calculations, e.g. for tungsten, are not available at this stage.

## 6. Conclusions

In this paper we have applied our recent theory of the kinetics of field ionization, field desorption and field evaporation to study field evaporation of tungsten. We have developed a perturbative method to calculate diabatic states from adiabatic ones. We find good agreement of the field dependence of the activation barrier with experimental data. We also find that the prefactor in the ion yield increases initially (up to  $4.5\text{V}/\text{\AA}$  for tungsten) due to an rapid increase in the ionization probability and then decreases with increasing field strength due to changes in the surface potential. There is some discrepancy in the absolute value which must be resolved by better experiments and by a better theory. For the latter, we are currently adopting a cluster programme based on the spin density functional theory to more properly account for charged species by a better treatment of Coulomb effects. We will then also present results for other metals to hopefully stimulate further experiments.

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Table 1

Field dependence of the activation barrier,  $Q$ , and the prefactor,  $av$ , experimental data from Ref.[7]. Also, the ground state frequency  $\nu_0$  and the excited frequency  $\nu_i$  for which  $h\nu_i=Q$ ; for details see text.

Field (V/Å)	Q(ev)		$k_0(\text{sec}^{-1})$		$\nu_0(\text{sec}^{-1})$	$n_i$	$\nu_i=(2n_i+1)\nu_0$ ( $\text{sec}^{-1}$ )
	exp.	calc.	exp.	calc.			
3.0	-	1.85	-	$1.01 \times 10^{14}$	$2.92 \times 10^{12}$	99	$4.58 \times 10^{14}$
3.50	-	1.72	-	$1.83 \times 10^{14}$	$4.93 \times 10^{12}$	55	$5.47 \times 10^{14}$
4.0	-	1.42	-	$2.33 \times 10^{14}$	$4.55 \times 10^{12}$	49	$4.54 \times 10^{14}$
4.5	-	1.22	-	$2.93 \times 10^{14}$	$4.62 \times 10^{12}$	41	$3.78 \times 10^{14}$
4.70	0.90	1.17	$3 \times 10^{16}$	$2.76 \times 10^{14}$	$4.52 \times 10^{12}$	37	$2.86 \times 10^{14}$
4.93	0.60	0.85	$1 \times 10^{13}$	$2.60 \times 10^{14}$	$4.00 \times 10^{12}$	30	$2.11 \times 10^{14}$
5.10	0.52	0.58	$8 \times 10^{12}$	$2.21 \times 10^{14}$	$3.51 \times 10^{12}$	24	$1.58 \times 10^{14}$
5.30	0.35	0.41	$7 \times 10^{11}$	$2.25 \times 10^{14}$	$3.17 \times 10^{12}$	18	$1.10 \times 10^{14}$
5.47	0.31	0.31	$7 \times 10^{11}$	$2.06 \times 10^{14}$	$2.83 \times 10^{12}$	15	$8.30 \times 10^{13}$
5.72	0.20	0.20	$3 \times 10^{11}$	$1.66 \times 10^{14}$	$2.68 \times 10^{12}$	10	$5.37 \times 10^{13}$
5.92	0.12	0.12	$4 \times 10^{11}$	$5.46 \times 10^{13}$	$2.64 \times 10^{12}$	7	$3.82 \times 10^{13}$



# Figure Captions

Fig.1: Adiabatic ( $V_i$ ) and diabatic ( $W_{ii}$ ) potential energy curves and schematic drawing of noninteracting ( $\phi_a$  and  $\phi_m$ ) and interacting ( $\phi_g$  and  $\phi_e$ ) orbitals to illustrate the discussion around equations (17-18).

